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Contributing sources to baseflow in pre-alpine headwaters using spatial snapshot sampling

Benjamin M. C. Fischer[1], Michael Rinderer[1], Philipp Schneider[1], Tracy Ewen[1], and Jan Seibert[1&2]

[1] Department of Geography, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland Tel.: +41-446355227, Fax.: +41-446356841, corresponding author: benjamin.fischer@geo.uzh.ch

[2] Department of Earth Sciences, Uppsala University, Sweden

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ABSTRACT

Mountainous headwaters consist of different landscape units including forests, meadows and wetlands. In these headwaters it is unclear which landscape units contribute what percentage to baseflow. In this study, we analysed spatiotemporal differences in baseflow isotope and hydrochemistry to identify catchment-scale runoff contribution. Three baseflow snapshot sampling campaigns were performed in the Swiss pre-alpine headwater catchment the Zwäckentobel (4.25 km^2) and six of its adjacent subcatchments. The spatial and temporal variability of δ^2H, Ca, DOC, AT, pH, SO_4, Mg, and H_4SiO_4 of streamflow, groundwater and spring water samples was analysed and related to catchment area and wetland percentage using bivariate and multivariate methods. Our study found that in the six subcatchments, with variable arrangements of landscape units, the inter- and intra catchment variability of isotopic and hydrochemical compositions was small and generally not significant. Stream samples were distinctly different from shallow groundwater. An upper spring zone located near the water divide above 1400 m and a larger wetland were identified by their distinct spatial isotopic and hydrochemical composition. The upstream wetland percentage was not correlated to the hydrochemical streamflow composition, suggesting that wetlands were less connected and act as passive features with a negligible contribution to baseflow runoff. The isotopic and hydrochemical composition of baseflow changed slightly from the upper spring zone towards the subcatchment outlets and corresponded to the signature of deep groundwater. Our results confirm the need and benefits of spatially distributed snapshot sampling to derive process understanding of heterogeneous headwaters during baseflow.

1. INTRODUCTION

Despite their importance for water resources, headwaters are still largely unmeasured (Bishop et al., 2008). This is especially true for mountainous headwaters where hydrological and hydrochemical observations are often difficult and thus, rare. Many mountainous headwaters are characterized by high amounts of precipitation, steep gradients, shallow soils and a mosaic of different landscape units such as forests, meadows and wetlands. Along the steep and deeply incised mountainous stream channels the riparian zone is generally missing (Sidle et al., 2000). For these heterogeneous mountainous headwaters it is still not fully clear which landscape units predominantly contribute to streamflow, and in particular sustain baseflow. Mountainous headwaters can contribute significantly to downstream runoff and in particular to baseflow (Tetzlaff and Soulsby, 2008). It is therefore important to understand where and how baseflow is generated to be able to make predictions on how baseflow might be affected by climate or land-cover changes. Besides baseflow quantity, water quality is also controlled by the pattern of different landscape units. To predict potential changes, it is important to understand water sources and transit times along the various flow paths. Tracer approaches are commonly used to study sources and flow paths of water (Barthold et al., 2010; Christophersen and Hooper, 1992; Hrachowitz et al., 2011; Inamdar et al., 2013; Lu, 2014; Penna et al., 2014a; Rodgers et al., 2005; Soulsby et al., 2007).

Of the different environmental tracers, the isotopes ^{2}H and ^{18}O have been found to be especially useful to identify sources of streamflow based on differences in the isotopic composition of the sources, e.g., rainfall and groundwater (Hrachowitz et al., 2011b; Tetzlaff and Soulsby, 2008). Hydrochemical tracers such as Ca or DOC, on the other hand, provide information on flow pathways as the concentrations depend on what the water encounters on its way from rain to stream (Inamdar et al., 2013; James and Roulet, 2006; Likens and Buso, 2006).

Streamflow integrates water from different sources. A common approach to study spatial variations in runoff contribution during streamflow is by synoptic, spatially distributed sampling to determine the isotopic and hydrochemical composition of water at various locations throughout a catchment (Fröhlich et al., 2008; Tetzlaff and Soulsby, 2008). Several studies have used baseflow snapshot campaigns to obtain information about spatial patterns of major baseflow controls. Temnerud et al. (2007), for instance, analysed the mixing of TOC (total organic carbon) along the stream network in a boreal catchment and found that the decrease of variability with scale could not be explained by mixing alone, but was a result of the spatial pattern of landscape units. Likens and Buso (2006) mapped the hydrochemical patterns of the Hubbard Brook Experimental Forest during two snapshot campaigns and found minor changes between the two seasons, but a large change in hydrochemistry along the stream network. Here, hydrochemical patterns were attributed to differences in vegetation, geologic substrates and wetland areas. Other studies found soil depth (Buttle et al., 2004; Kosugi et al., 2006) or active zones of seeping deep groundwater (Asano et al., 2009; Zimmer et al., 2012) to be important factors for baseflow generation. However, the importance of different spatial controls varies with geographic settings and especially steep pre-alpine regions with high precipitation amounts (P > 2000 mm year^{-1}) are not fully understood yet.

In this study we conducted three baseflow snapshot sampling campaigns in a steep and wet pre-alpine headwater and used the observed isotopic and hydrochemical signatures to assess which sources contribute to baseflow. We asked whether any spatial patterns of streamwater composition could be observed and whether there was any relation to (sub)catchment landscape units. In particular we addressed the role of wetlands in these wet headwater catchments.

2. MATERIALS & METHODS

2.1 STUDY AREA

The Zwäckentobel (4.25 km^2) is a Swiss pre-alpine headwater located in the Alptal 40 km south of Zurich (see Figure 1a). The south-north oriented catchment consists of approximately ten perennial streams. In the Erlenbach subcatchment (WS04) long-term observations of discharge and different hydrochemical variables exist (Hegg et al., 2006; Schleppi et al., 2006). Subcatchment characteristics such as area (km^2), altitude (m), slope (°) were derived from a digital elevation model (DEM; 2 m resolution; Swisstopo, 2002) using the Whitebox Geospatial Analysis-D8 flow pointer tool (Lindsay, 2009) (Table 1). All subcatchments have alternating steep slopes of more than 20° and flatter areas along the main axis, originating from erosion deposits such as soil creep and landslides.

The geology of the region is tertiary flysch consisting of different calcarius sedimentary layers of schist, marl or sandstone (Hsü and Briegel, 1991) (Figure 1b). Ontop of the flysch parent material are shallow and creeping gleysols (0.5-2.5 m in depth). These gleysols consist of a B_g-horizon with high silt and clay content and the A-horizon of 20-50 cm Muck or Mor humus (Feyen et al., 1996). The clay layer has low matrix permeability but high drainage capacity in macropores (see Feyen et al. (1996) for a more detailed soil description). The land cover of the Zwäckentobel is light to dense spruce forest, moorland or meadows. During the summer months, the meadows of WS18, WS19 and the upper part of WS04 and WS07 are used as alpine pastures. The different land cover were delineated from an aerial photo (Swiss Federal Office of Topography, 2005) and divided into three classes: forest, partly forested and meadow (Figure 1c). Wetlands were derived from the available Swiss Cantonal wetland inventory (Swiss Federal Office for Environment, 2007).

The Zwäckentobel has a humid-temperate climate with a mean annual temperature of 6°C (Feyen et al., 1996). The annual precipitation is 2300 mm year^{-1} and is relatively equally distributed but slightly skewed to the summer season (Turowski et al., 2009). On average there is precipitation on almost every second day. About one third of the annual precipitation falls as snow (Stähli and Gustafsson, 2006). During rainfall events, streams respond quickly and flow increases by several orders of magnitude, but returns to baseflow within approximately one day.

2.2 FIELD SAMPLING DESIGN

Three spatially distributed snapshot campaigns were carried out: Campaign C-1 on 19 November 2010, at the end of the summer season had an early snow cover and was representative of early winter baseflow conditions; C-2 on 7 June 2011, shortly after all snow cover had melted was characterized by short dry spells and higher groundwater levels; and C-3 on 18 October 2011, in autumn, had longer dry spells with lower groundwater levels (see Figure 2). These dates were chosen to represent the preceding hydro-meteorological period, i.e., spring with typically high groundwater storage (C-2) and autumn with typically low groundwater storage (C-1 and C-3). The campaigns were planned such that the system was in a baseflow state with at least two antecedent days without precipitation (Figure 2) ensuring stable flow conditions to more easily identify sources (Temnerud et al., 2007).

Due to frequent precipitation events it was important to collect all samples in one day. Therefore, the number of sampling locations was restricted to 110 and distributed discharge measurements could not be performed for practical reasons. The actual number of samples taken was less than the 110 predefined sampling points as there was too little or no water at all at some of the points (Table 1). During each campaign five sampling teams visited each 10-20 sample points with a handheld GPS (Garmin GPSMAP 60CS, field accuracy ±8m). For each sampling location, two grab water samples were taken; 20 ml for stable isotope analyses (20 ml glass vial with cap and additional Teflon/rubber septum) and 250 ml for hydrochemical analyses (250 ml PE bottle with cap).

The sampling locations were selected by following the stream network of the different subcatchment outlets upslope to the water divide. Perennial key locations were chosen such as confluences of different branches (n=65 of which eight samples were taken along an artificial drainage ditch from a wetland (W) within WS04), springs (n=29) and groundwater wells (n=16) (Figure 1a). Groundwater samples were taken from fully-screened wells with an average depth of about 1 m (for details on the groundwater observation network see Rinderer et al., 2014).

Similar to the subcatchment characteristics, for every sampling location different upslope controlling landscape features were derived such as the area (km^2), altitude (m), slope (°) and, topographic wetness index within a Geographic Information System (GIS) framework. Additionally, for each sampling location the upslope percentage of forest, meadow and wetlands were derived from the land use map. The percentage of the different types of geology and shallow soils was derived from the geological map with an additional DEM-analysis where slopes >20° were set to a soil depth of 1 metre. This was then spot checked with a hand auger in the field and resulted in an estimate of the shallow soil information (depth larger than or less than 1 m).

2.3 LABORATORY METHODS

For the isotopic composition the water samples were analysed in the stable isotope laboratory of the University of Zurich, Department of Geography. The samples were filtered prior to analysis with a 0.45 µm filter (25 mm PTFE Syringe Filter, Simplepure USA) from which 1 ml was pipetted in a vial (1.5 ml 32×11.6 mm screw neck vials with cap and

PTFE/silicone/PTFE septa). Samples were analysed with a Cavity Ring-Down Spectroscope-Picarro L1102-i Liquid Analyser (1st generation analyser with a manufacturer's precision of $\delta^2H < 0.5‰$ and $\delta^{18}O < 0.1‰$) and the analysis scheme of Penna et al. (2010).

The 250 ml water samples were analysed for hydrochemical variables Ca, DOC, (electrical conductivity (CT), pH, alkalinity (AT), total hardness (TH), Cl, NO_3, SO_4, Na, K, Mg, and H_4SiO_4) at the laboratory of the Swiss Federal Institute of Aquatic Science and Technology (EAWAG; see Table 2 for instruments used). All samples were filtered prior to analysis with a 0.45 µm filter (Ø 47 mm cellulose filter paper, Whatman Germany).

2.4 DATA ANALYSIS

The three snapshot campaigns resulted in datasets consisting of selected isotopic and hydrochemical variables. A selection of isotopic and hydrochemical variables (δ^2H, Ca, DOC AT, pH, SO_4, Mg and H_4SiO_4) was made based on their value for identifying processes, detection limit of the instruments, and the correlation between different variables to avoid redundancies. For each campaign, the different variables were summarized for stream samples taken in the subcatchments (WS04 to WS19), at the different subcatchment outlets (O), in groundwater wells (G) and at springs (S). Spatiotemporal differences were tested with the Tukey's honestly significant difference criterion $\alpha = 0.05$ (Hochberg and Tamhane, 2008) for different variables and campaigns. The spatial variability of different hydrochemical variables and sampling locations were visually assessed by representing the streamflow, geology, organic matter (δ^2H, Ca and DOC respectively) as sampled in space. Changes in variability were further assessed by expressing each sample point δ^2H, Ca or DOC as a function of different upslope controlling landscape features such as the catchment area, altitude, slope, topographic wetness index, land use (forest, meadow and wetland), geological facies and shallow soils.

Hydrochemical mixing was further examined with bivariate solute diagrams, and a PCA was performed to investigate the spatiotemporal patterns of the isotopic and hydrochemical variables (δ^2H, Ca, DOC, AT, SO_4, Mg, and H_4SiO_4). The resulting patterns for each campaign were compared to give an indication of hydrochemical compositions. From the chosen sampling design (springs, stream and groundwater well samples) only two end-members were available to explain streamflow. Therefore instead of a full geographical end-member mixing analysis (EMMA), the end-members groundwater from wells and springs were used as an explorative element to explain the contribution to streamflow. The median values of sampled end-members were projected together with their upper and lower quartiles into the bivariate solute diagrams and PCA-biplots.

A summary of the data and spatial representation for the campaign C-1 can be found in the supplementary material, but because of the snow cover and the reduced number of sampling points, this campaign C-1 is not included in the analyses presented in this paper.

3. RESULTS

3.1 VARIABILITY IN ISOTOPE AND HYDROCHEMICAL CONCENTRATIONS

Figure 3a shows the variability of δ^2H, Ca and DOC for each campaign (C-2, C-3) and for stream samples of the subcatchments (WS04 to WS19), subcatchment outlet samples (O), groundwater wells (G) and spring samples (S). Figure 3b shows the same analysis for the remaining hydrochemical variables: AT, pH, SO_4, Mg, and H_4SiO_4. The results of significance tests are indicated in italic letters inside each box for campaigns, and on top of each box subcatchments and outlets referring to: (I) the spatial comparison for each source (O, G and S) and subcatchment WS04 to WS19; (II) the intra-comparison of watershed samples to the respective subcatchment outlets; where mixing of each subcatchment towards the subcatchment outlet was separately assessed with the Wilcoxon signed rank test ($\alpha = 0.05$; shown as a grey box), and (III) a comparison for each snapshot campaign (C-2, C-3).

For δ^2H, the spatial comparison of the different groups (WS04-WS19, O, G and S) shows for groundwater, which had been sampled from wells, significantly lower δ^2H values compared to stream samples from WS19 and the outlets for campaign C-2. For C-3 on the other hand, there were no significant differences (Figure 3a, top) and only the outlet of WS10 was significantly different to the internal sampling points. For the comparison between campaigns C-2 and C-3, there were significant differences with enriched δ^2H for WS04, WS10, WS18, O, G and S in C-3 compared to C-2.

For campaign C-2 the spatial comparison shows significantly higher Ca concentrations for groundwater from wells compared to stream samples from WS04, WS10, WS19, the outlets and the springs. For C-3 the groundwater from wells had significantly higher concentrations compared to the stream samples from WS04 and outlets (Figure 3a, middle). For the comparison between campaigns, the concentrations were significantly lower for C-3 compared to C-2 for WS04, WS18 and G whereas the concentrations were significantly higher for C-3 compared to C-2 for WS10, O and S.

For DOC, the spatial comparison shows significantly higher concentrations for groundwater from wells compared to the stream samples of WS04, WS07, WS10 and the springs for C-2 (Figure 3a, bottom). For C-3 the groundwater from wells had significantly higher concentrations compared to the springs. In both C-2 and C-3, stream samples of WS04 had the largest interquartile range (IQR). For the intra-comparison to the outlet, a significant difference was found for WS10. For the comparison between campaigns, there was a higher concentrations and significant difference for WS19 and O, G and S for C-3 compared to C-2.

For each of the remaining hydrochemical variables, the IQR among groundwater samples was high for AT, Mg and H_4SiO_4 for both C-2 and C-3 (Figure 3b). Groundwater samples from wells were significantly different for C-2 from WS04, WS10, and samples from O and S were significantly different for AT, SO4 and H_4SiO_4. For springs, IQR was high for SO_4 and H_4SiO_4 in C-2 and C-3 and high for AT in C-3. The outlets showed less variability for AT, SO_4, Mg and H_4SiO_4 during both C-2 and C-3. For the subcatchment variability there were no significant differences found except for SO_4 which had a high IQR in stream samples of WS04 and WS10 in C-2 (significantly different) and C-3. For pH, only groundwater from wells differed significantly while other differences were near or within the instrument precision of ±0.05 and therefore not significant. For the intra-comparison to outlets, only, SO_4 and Mg for WS04 in C-2 and C-3 show a significant difference, as well as SO_4 for stream samples of WS07 in C-3. For the differences between campaigns, there were no significant differences found.

Ca, DOC, AT and H_4SiO_4 in groundwater from wells and spring samples were quite variable during the two campaigns (C-2, C-3), whereas the outlets show less variability overall. Additionally, samples from groundwater wells had a distinct composition with higher Ca, DOC, AT and low SO_4 concentrations while springs had high Ca, SO_4, H_4SiO_4 but low DOC.

3.2 ISOTOPIC AND HYDROCHEMICAL PATTERNS

The δ^2H, Ca and DOC composition varied in space and time (Figure 4). For δ^2H (top row) in sampling campaign C-2 the springs near the water divide had generally lighter δ^2H compared to stream samples, with some exceptions in WS07, WS10 and WS19. A more variable pattern of δ^2H in stream, groundwater wells and spring samples occurred in C-3. Large differences can be seen in δ^2H between C-2 and C-3 with the exception of spring S-55. Generally the springs near the water divide had more depleted δ^2H values compared to the stream samples, which had more enriched values δ^2H downslope.

The spatial patterns of Ca (middle row) remained similar for the three campaigns. Springs and groundwater well samples of area I had higher Ca concentrations compared to most stream samples. This area I lies above 1400 m and can be defined as an "upper spring zone" (see Figure 1a). In WS04 and WS07 the Ca concentrations decreased from the springs near the water divide from 80 mg L^{-1}, towards the subcatchment outlet to 60 mg L^{-1}. Compared to WS04 and WS07 the subcatchments WS10 and WS11 had 5-10 mg L^{-1} lower Ca concentrations.

The spatial patterns of DOC (bottom row) showed a similar pattern for the campaigns with increasing concentrations from the upper springs in area I (1.3 mg L^{-1}) towards the catchment outlet (2.8 mg L^{-1}). DOC values of some springs had 1-2 mg L^{-1} higher concentrations (see S-55 and S-81). Water samples from groundwater wells tended to have DOC concentrations of 5 up to 7 mg L^{-1}. In both C-2 and C-3 a tributary in WS04, which is a drainage ditch from a wetland (see area II), stood out by having distinctly different concentrations with DOC concentrations similar to groundwater well samples (7 mg L^{-1}) but approximately 5 mg L^{-1} higher compared to springs and stream samples. The δ^2H values observed for this tributary were 4‰ higher compared to the main stream and Ca concentrations were approximately 20 mg L^{-1}, which was 20-50 mg L^{-1} lower than the other stream, spring and groundwater well samples. Furthermore WS18 had slightly lower Ca concentrations and higher DOC concentrations with respect to the neighbouring spring area I.

3.3 CONTROLLING LANDSCAPE CHARACTERISTCS

The effect of mixing along the stream network for the selected variables δ^2H, Ca and DOC is shown by expressing the different concentrations as a function of their catchment area and wetland percentage in Figure 5. The variability of δ^2H, Ca and DOC composition decreased from the springs (approximate upslope area 0.001 km^2) towards 0.2 km^2 where several first order streams from springs come together and defined the upper spring zone above 1400 m. Below this upper spring zone the streamflow composition changed only slightly towards the subcatchment outlets. Along the stream network of WS04 the variables δ^2H, Ca and DOC showed a distinctly different composition between the main stream (black lines, Figure 5), and its tributaries from wetlands (grey lines with large symbols, Figure 5). The δ^2H of the main stream increased slightly towards the subcatchment outlet (C-2; -80 to -76‰ and C-3; from -74 to -70‰), Ca concentrations decreased (C-2 and C-3; from 80 to 60 mg L^{-1}) while DOC increased (C-2 and C-3; from 1.3 to 2.8 mg L^{-1}). The tributary draining a wetland (area II in Figure 3) had high δ^2H, low Ca and high DOC concentrations. Furthermore spring S-9 was distinctly different in its signature (enriched δ^2H, higher Ca and marginally higher DOC concentrations) compared to neighbouring springs in WS04.

The role of wetlands as a potential controlling element on the hydrochemistry was further examined by expressing Ca and DOC as a function of upslope wetland percentages (see Figure 6). For both C-2 and C-3 the tributaries of WS04 had lower Ca (20-50 mg L^{-1}) and higher DOC concentrations (6 mg L^{-1}) compared to most streams (Ca 65 mg L^{-1} and DOC 3 mg L^{-1}) and springs (Ca >70 mg L^{-1} and DOC 2 mg L^{-1}). Exceptions were groundwater samples from wells (Ca >70 mg L^{-1} and DOC 7 mg L^{-1}) and springs of WS18 with slightly increased DOC concentrations (4 mg L^{-1}) as compared to other springs.

The hydrochemical variables Ca and DOC were selected as representing geology and organic matter respectively, to assess the mixing of the different water samples (Figure 7). The bivariate representation of Ca and DOC of C-2 and C-3 showed that most stream samples of the different subcatchments had a similar hydrochemical composition and were clustered near Ca ±60 mg L^{-1} and DOC ±2.5 mg L^{-1}. These samples were similar to deep groundwater from springs (S) from near or from bedrock with high Ca but low DOC concentrations. Groundwater samples from observation wells (G) had characteristic concentrations for the integrated soil profile, i.e., shallow groundwater with high Ca and average DOC concentrations. Stream samples from WS04, draining a wetland (Figure 5 and 6), were significantly different from other samples for all variables in C-2 and C-3, and had their own characteristic, e.g., enriched δ^2H values as well as lower Ca and higher DOC concentrations. Even though this is a low number of sampling points with a clear wetland signature, these available samples were a first indication of a third end-member from wetlands (W). The median value of these possible end-members of wetlands (W), groundwater wells (G) and springs (S) were added to the bivariate representation of Ca and DOC (Figure 7) to indicate possible runoff sources during baseflow. For C-2 most stream samples had signatures of the deep groundwater from springs while in C-3 some samples of WS18 and WS19 shifted towards the wetland end-member. In both C-2 and C-3 the samples that were identified as tributaries in WS04 draining a wetland (Figure 5 and 6), had higher DOC concentrations and therefore a wetland signature. These results are consistent with the descriptive statistics and spatial and longitudinal representation of different variables (shown in Figures 3 to 5), indicating spatial differences and potential end-members (springs, groundwater wells and wetlands).

The isotopic and hydrochemical dataset was additionally explored with a PCA for sampling campaign C-2 and C-3 (Figure 8). From the Kaiser's rule (Kaiser, 1960) it followed that for the PCA, two principal components were sufficient to explain between 60% (C-2) and 80% (C-3) of the variance. The different isotopic and hydrochemical factor loadings were located in different quadrants (numbered with roman numerals, see Figure 8). From the scores of PCA of sampling campaigns C-2 and C-3, it appeared that the different sampling points for each subcatchment (grouped in different quadrants), were correlated with different isotopic and hydrochemical variables. The sampling points of the smaller subcatchments WS10 and WS11 were in quadrant II while WS18 and WS19 were in quadrant III. The larger subcatchments WS04 and WS07 were similarly distributed over quadrant I, II and IV. Similar to the bivariate representation of Ca and DOC for C-2, the different samples were closer together and showed an increase in spread for C-3. The possible end-members W, G and S (observed in the bivariate analysis) were added by their median values to the PCA-biplot. For both campaigns, WS04 and WS07 had a dominant spring and wetland signature while WS10 and WS11 were marked by a spring signature. WS18 and WS19 were bounded by the end-member groundwater from wells and wetlands. Compared to bivariate representation in the PCA-biplot more samples were not bound by the three different end-members of spring, groundwater wells and wetland.

4. DISCUSSION AND CONCLUSIONS

4.1 SPATIOTEMPORAL VARIABILITY OF HYDROCHEMICAL VARIABLES

We demonstrated with three snapshot campaigns during baseflow that such an analysis of hydrochemical variables and isotopic composition can be applied to steep and wet pre-alpine headwaters with different landscape units including forests, meadows and wetlands. Observing isotopic and hydrochemical signatures dynamics during baseflow, we investigated which sources contribute to baseflow. We further identified the spatial patterns of streamwater composition and their relation to (sub)catchment landscape units and stream chemistry. An additional focus was on understanding the role of wetlands in this type of wet headwater catchments.

In the analysis of the spatiotemporal variability for selected isotopic (δ^2H) and hydrochemical (Ca, DOC, AT, pH, SO_4, Mg and H_4SiO_4) components, the variability of the concentrations was small and statistically not significant within and between these subcatchments, despite the differences in landscape characteristics of the six adjacent subcatchments. Streamwater samples at the subcatchment outlets, however, were more similar to springs than to groundwater from observation wells.

From the selected variables, the combination δ^2H, Ca and DOC proved to be most useful for distinguishing different sources. Although we observed the influence of geology on the hydrochemical composition of streamwater, in contrast to findings of Soulsby et al. (2007), the hydrochemical variables Ca, Mg and H_4SiO_4 gave no further information to distinguish between the three geological flysch facies. The spatial difference in SO_4 concentrations between the different subcatchments could neither be explained with a geological map, or as indicated by Keller et al. (1989), by atmospheric deposition. From our observations it is likely that during baseflow subcatchments with high SO_4 concentrations are dominantly fed by deep groundwater from springs with slightly higher SO_4 concentrations compared to shallow groundwater and wetlands. An additional increase in SO_4 concentrations of WS04 and WS10 are likely due to both their steep and erosive stream networks. This additional weathering of flysch layers containing $CaSO_4$ (anhydrite) might have increased the concentration of SO_4 (Campbell et al., 1995). This is also in agreement with low SO_4 concentrations for the flatter more stable stream network of WS07 and WS19. These first results could be further examined in a more detailed study to gain insight into the poorly understood and complex interaction of SO_4 from atmosphere, weathering, terrestrial processes and limnology, as previously stated by Campbell et al. (1995). Studies with different geologies such as granitic (Likens and Buso, 2006; Zimmer et al., 2012) or schist (Asano et al., 2009) had two orders of magnitude lower Ca concentrations compared to the Zwäckentobel (Keller et al., 1989; Zobrist, 2010). The Ca rich geology resulted in that all streamwater samples were highly buffered (pH near 8.0). This blurred potential differences in pH between different landscape units including wetland, pastures and forest. Comparing our Ca concentrations with observations made by Keller (1990) and Keller et al. (1989), who studied hydrochemical variables at the outlet of WS04 together with six additional headwaters (below 1 km^2) in the larger Alptal catchment (47 km^2) had spatial variabilities of baseflow concentrations for Ca, of 50-80 mg L^{-1}; H_4SiO_4, of 1-3 mg L^{-1}; and SO_4 of 3-25 mg L^{-1}. These concentrations corresponded to the spatial variability, observed in our adjacent subcatchments, WS04-WS19, which implies similarities in baseflow generation. Instead, Schleppi et al. (2006) showed the long-term temporal variability of Ca for WS04 (for 15 years of weekly discharge with proportional sampling at the catchment-scale) and found that Ca was approximately 60 mg L^{-1} during baseflow while for higher flows the concentration decreased exponentially to 20 mg L^{-1}. This long-term temporal variability is of the same order of magnitude as the spatial variability of deep groundwater and wetlands during baseflow found in our study. This overlap of the sampled concentrations are a potential source of error when used in hydrograph separation to distinguish between different sources, e.g., pre-event water from groundwater and wetlands (Ca >50 and 20 mg L^{-1}, respectively) compared to event water (Ca 0 mg L^{-1}).

Spatial differences of δ^2H, Ca and DOC became visible by mapping the measured chemical variables to the respective sampling locations. Different landscape units with water of a distinct isotopic and hydrochemical signature could be identified: a tributary, i.e., a drainage ditch, from a wetland in WS04, and the upper spring zone that was near the water divide located above 1400 m. The spatial representation of δ^2H, Ca and DOC also helped to visualise changes in concentrations along the stream and distinguish deep groundwater from springs which were connected to different flowpaths, as in the case of springs S-81, S-55 and S-9.

4.2 THE ROLE OF LANDSCAPE UNITS IN SUSTAINING BASEFLOW

Several studies found evidence of hydrochemical changes along the stream network, e.g., Asano et al. (2009) pointed to the signal propagation along the longitudinal stream network while Zimmer et al. (2012) discussed the dominance of small active sources from upstream areas of a catchment. Other studies found relations with different landscape characteristics (Frisbee et al., 2011; Rodgers et al., 2005). Temnerud et al. (2007) stated that the dampening of the hydrochemical variability originates not from conservative mixing but from a structured mosaic of landscape units. Our study supports these previous findings. From the isotopic and hydrochemical variables we gained insight into the baseflow generation processes and the contributing sources in steep and wet pre-alpine headwaters with a heterogeneous landscape.

The water composition (δ^2H, Ca and DOC) varied considerably. This variability was examined by representing each variable according to their sampling point's upstream landscape features such as catchment area, altitude, slope, topographic wetness index, land use (forest, meadow and wetland), geological facies and shallow soils. However, only a clear relation of δ^2H, Ca and DOC as a function of catchment area was found, where the variability at catchment scales of 0.2 km^2 was reduced (analysis of the other landscape features showed no strong relationships). The upslope scale of 0.2 km^2 coincided with the observed upper spring zone. At scales larger than 0.2 km^2, i.e., outside the upper spring zone, the hydrochemical composition of the main stream increased or decreased little and remained more similar to the isotopic and hydrochemical composition from the upper spring zone near the water divide. In the case of WS04, the upper spring zone had the lightest δ^2H composition, with heavier δ^2H concentrations downstream and with decreasing altitude. In contrast, wetlands had enriched δ^2H, indicating different water and flowpaths compared to the spring zone or groundwater from wells. Comparing the differences in wetland and stream samples, it is likely that due to the continued saturated state, water in wetlands is younger with shorter transit times compared to "older" water from the steeper slopes, which was also observed by Inamdar et al. (2013). High Ca concentrations in the upper spring zone originate from deep groundwater which dissolves the carbonate bedrock. Once at the surface and in the stream, stabilizing processes (e.g., chemical precipitation) and mixing with water of lower concentration may have led to decreasing Ca concentrations further downstream. Another typical hydrochemical characteristic of deep groundwater from springs was the low DOC concentrations. DOC concentrations increased and Ca concentrations decreased slightly downstream but maintained a signature similar to low DOC and high Ca concentrations from springs, i.e., deep groundwater. At confluences with tributaries from wetlands, the composition of δ^2H, Ca and DOC changed little and any changes were likely due to only minor contributions from the side branches to baseflow in the main stream, i.e., the wetlands were less connected. This was supported by Ca or DOC concentrations of sampling locations represented according to their upstream wetland percentage. In a situation where wetlands and other areas contribute equally to baseflow the different sampling points would resemble a line between low wetland percentage with high Ca and low DOC concentrations (i.e., wetland 20%; Ca 75 mg L^{-1}; DOC 2 mg L^{-1}) and high wetland percentage with low Ca and high DOC concentrations (i.e., wetland 100%; Ca 20 mg L^{-1}; DOC >6 mg L^{-1}). From our sampling design most sampling locations, including sites with high wetland percentage, had high Ca and low DOC concentrations and we concluded that their streamwater originated from runoff sources other than wetlands. The DOC concentrations in this study were in the same range as at other headwaters (James and Roulet, 2006; Likens and Buso, 2006; Tetzlaff and Soulsby, 2008); but one order of magnitude lower compared to Swedish headwaters (Temnerud et al., 2007).

Bivariate solute diagrams and multivariate principal component analysis are established methods to distinguish between different spatiotemporal patterns of streamwater composition and characterise specific geographic water sources of different catchments in relation to their multiple variables (Barthold et al., 2010; Christophersen and Hooper, 1992; Fröhlich et al., 2008). In our study the bivariate representation of Ca and DOC was useful to identify three runoff sources: deep groundwater from springs, shallow groundwater and wetlands sampled in the drainage ditch of WS04. Although our sampling design had only few stream samples that were directly sampled and a distinct wetland signature (low Ca, high DOC), the bivariate representation with end-members gave a first impression of the origin of runoff during baseflow. Most samples were grouped together near the hydrochemical composition of deep groundwater from springs located near the water divide. Only few streamwater samples showed a signature that was similar to the samples from wetlands or shallow groundwater from observation wells. For the bivariate representation of Ca and DOC the observations were largely bounded within the degree of uncertainty by three end-members of groundwater wells (shallow groundwater), springs (deep groundwater) and wetlands.

In contrast to the bivariate representation of Ca and DOC, the PCA-biplot gave more insight into differences of the spatial isotopic and hydrochemical. Fröhlich et al. (2008) observed that different subcatchments can have a unique hydrochemical composition at a larger catchment scale (692 km^2). Similarly, (Hrachowitz et al. 2011) showed this for a semi-arid catchment and (Lu, 2014), for a volcanic catchment. From the PCA-biplot we made similar observations for the studied headwaters. Subcatchments had distinct isotopic and hydrochemical compositions, where neighbouring subcatchments formed pairs with comparable hydrochemical compositions: WS04 and WS07, WS10 and WS11 and WS18 and WS19. These spatial patterns of isotopic and hydrochemical composition were coherent and combined the analyses (boxplot and bivariate representation of Ca and DOC) into one analysis to give a comprehensive overview of the multivariate data (δ^2H, Ca, DOC AT, pH, SO_4, Mg, and H_4SiO_4). Compared to the bivariate representation with end-members, for the PCA-biplot, not all observations were bounded by the end-members. This might be due to the unique hydrochemical composition of subcatchments, with single or other (not sampled) end-members. Besides this limitation of the available end-members, these extreme signatures proved to be useful as a first indicator for baseflow runoff processes and source areas.

4.3 WIDER IMPLICATIONS ON PRE-ALPINE BASEFLOW

Pre-alpine headwaters with shallow soils and high precipitation respond quickly to rainfall and thus, therefore, according to Frisbee et al. (2011), a network-mixing model would be a valid conceptualisation of these systems. Shallow soils, however, have a limited aquifer while glacial valley bottom deposits can sometimes store groundwater from upslope areas and sustain baseflow (Tetzlaff and Soulsby, 2008). Other studies showed that during baseflow conditions the riparian zone acts as the main input to streamflow generation (Penna et al., 2014; Sidle et al., 2000). Our studied headwaters were lacking such a valley aquifer and riparian zone. We rather observed different spatially distributed baseflow generating zones similar to the work of Asano et al. (2009) and Zimmer et al. (2012), from the deep groundwater (perennial springs, in the upper spring zone near the ridge). Despite the shallow soils with limited storage capacity, deep groundwater seeped from fractures and fissures into the zero-order basin and fed the first order stream channels and this deep groundwater seemed to be permanently connected to the stream network. The C-2 and C-3 campaigns showed a seasonal change for stable isotopes reflecting water with longer transit times, whereas spatial patterns of the hydrochemistry remained mostly similar. Less than 10% of the groundwater and spring samples changed in their composition, presumably due to a connection with a different flowpath. Our findings confirmed the statement of Keller et al. (1989) who postulated that baseflow originates from deep percolating water from springs based on sampling at the catchment outlet. Uchida et al. (2005) made similar observations in steep, homogeneous and forested headwaters in Japan. Inamdar et al. (2013) found from changes in hydrochemistry that during seasonal drying over the summer (in dry conditions), portions of the drainage network were disconnected and did not contribute to streamflow. Contrary to this seasonal change in connectivity, our findings show that passive, in terms of being hydrologically less connected landscape units can also occur in rainfall dominated headwaters such as the Zwäckentobel catchment (2300 mm year^{-1}). The wetlands are prominent landscape units with large storage capacity and areal extent (30-60% of the subcatchment area) but during baseflow these features mostly act as passive units not significantly contributing to baseflow. Consequently, pre-alpine headwaters with similar climate, geology and topography are, during baseflow, not just the sum of different landscape units, but are rather dominated by the arrangement of connected (active) or disconnected (passive) landscape units as conceptualised by Sidle et al. (2000) and Ambroise (2004).

The Zwäckentobel headwater is dominated by deep groundwater from the upper spring zone near the water divide. The isotopic and hydrochemical composition does not change significantly during baseflow towards the catchment outlet. We cannot fully exclude that outside the upper spring zone (altitudes below 1400 m) deep groundwater or groundwater with a similar composition to the streamwater contributed to baseflow. From our analysis of δ^2H, Ca and DOC, it is more likely that the deep groundwater from the upper spring zone determines to a large extent the isotopic and hydrochemical signatures of baseflow contribution at the subcatchment outlet. Within the upper spring zone, as well as for other sampling locations, we could not distinguish between the isotopic and hydrochemical composition and different landscape units such as forest, meadows and wetlands. This might be partly due to sampling design and the chosen isotopic and hydrochemical variables. However, it is more likely that the dominance of active sources from the upper spring zone explains why we did not observe, with exception of catchment area and implicit altitude (represented by the stream network), any other relations between hydrochemistry and controlling landscape features. Nevertheless, these active contributing point elements, such as seeping deep groundwater from springs with passive features are indicators short and long flowpaths and transit times (Rodgers et al., 2005). Therefore, instead of a network-mixing model it is more likely that steep wet pre-alpine headwaters are better represented with a more complex "Tóthian", i.e., topography-energy driven flow model, as discussed by (Frisbee et al., 2011)

Hence, future studies in pre-alpine headwater catchments should focus not only on headwater mean transit times but as shown by Tetzlaff et al. (2014) on the transit times of water through the different contributing landscape units. Overall, our results confirm the usefulness need and benefits of spatially distributed snapshot sampling to increase spatial process understanding of heterogeneous headwaters during baseflow. These results underline the usefulness of nested and / or spatially distributed tracer studies to increase knowledge of the fundamental mechanisms and governing process of baseflow generation in headwater systems.

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Table 1 Sample number for the three snapshot campaigns of the Zwäckentobel outlet (ZT) and its subcatchments WS04 to WS19 with its topographic, geology and land use characteristics.

				SUBCATCHMENT						
			∑n	**ZT**	**WS04**	**WS07**	**WS10**	**WS11**	**WS18**	**WS19**
CAMPAIGN - SAMPLES	**C-1 (19.11.2010)**		46	1	7	14	12	5	0	7
	C-2 (07.06.2011)		82	1	16	20	16	8	6	15
	C-3 (18.10.2011)		84	1	24	20	14	7	8	10
TOPO-GRAPHY	**Area**		km^2	4.25	0.73	0.21	0.23	0.09	0.15	0.15
	Altitude	*max*	m	1656	1656	1656	1598	1583	1598	1598
		mean	m	1360	1342	1468	1432	1421	1476	1494
		min	m	1084	1109	1262	1276	1292	1351	1384
	Slope	*mean*	°	19	17	21	23	24	20	18
		max	°	56	49	47	53	45	42	43
GEOLOGY	**Waegitaler flysch**		%	29	64	16	0	0	0	0
	Wild flysch		%	17	29	42	0	0	0	0
	Schlieren flysch		%	54	7	42	100	100	100	100
	Shallow soils<1m		%	29	44	55	73	74	59	49
LAND USE	**Forest**		%	55	53	53	72	81	38	18
	Partly forested		%	21	22	27	14	10	10	1
	Meadow		%	24	25	20	14	9	52	81
	Wetland		%	29	33	28	23	21	57	51

Table 2 Overview of different variables and instruments used for stable isotope and hydrochemical analysis: electrical conductivity (CT), pH, alkalinity (AT), total hardness (TH), Chloride (Cl), nitrate (NO_3), sulphate (SO_4), Sodium (Na), Potassium (K), Calcium (Ca), Magnesium (Mg), Dissolved Organic Carbon (DOC) and Silicic acid (H_4SiO_4).

Variable	**Instrument**	**Manufacturer**	**Precision**
^2H & ^{18}O	Cavity Ring-Down Spectroscope-Picarro L1102-i liquid analyser	Picarro, Inc., USA	0.5‰ & 0.1‰ for (δ^2H & $\delta^{18}O$)
CT	Metrohm 712 conductometer	Metrohm Schweiz AG, Switzerland	2 µS cm^{-1}
pH AT	Metrohm 809 Titrando with pH-electrode		0.05 pH 0.1 mmol L^{-1}
TH	Metrohm 809 Titrando with ion selective electrode		0.1 mmol L^{-1}
Cl NO_3 SO_4	Metrohm 761 Compact IC with chem. Suppression with Metrosep A Supp 5 100/4 mm column		0.2 mg L^{-1} 0.1 mg L^{-1} 2.0 mg L^{-1}
Na K Ca Mg	Metrohm 761 Compact IC with chem. Suppression with Metrohm C 4 - 100/4.0 column		0.8 mg L^{-1} 0.3 mg L^{-1} 1.7 mg L^{-1} 0.8 mg L^{-1}
H_4SiO_4	Autoanalyser AA3, Bran+Luebbe and method no. G-177-96 (Methods of Seawater Analysis, K. Grasshoff, M. Ehrhard, K. Kremling 1983)	Bran and *Luebbe*, Germany	0.2 mg L^{-1}
DOC	Shimadzu TOC-V CPH	Shimadzu Corporation, Japan	0.2 mg L^{-1}

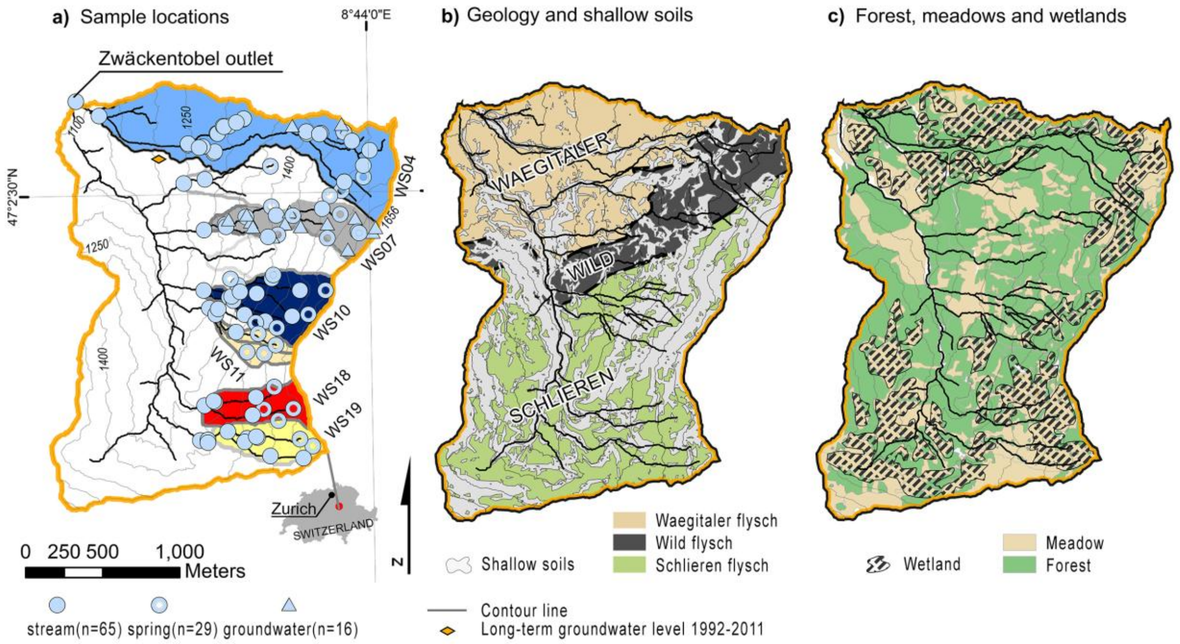

Figure 1 Maps of the Zwäckentobel with a) sampling locations in selected subcatchments WS04, WS07, WS10, WS11, WS18 and WS19, b) geology: three different types of flysch with shaded grey areas indicate shallow soils located on slopes >20° and c) land use: forest and meadows with shaded areas wetlands. Colours scheme Figure 1b and 1c from www.ColorBrewer.org.

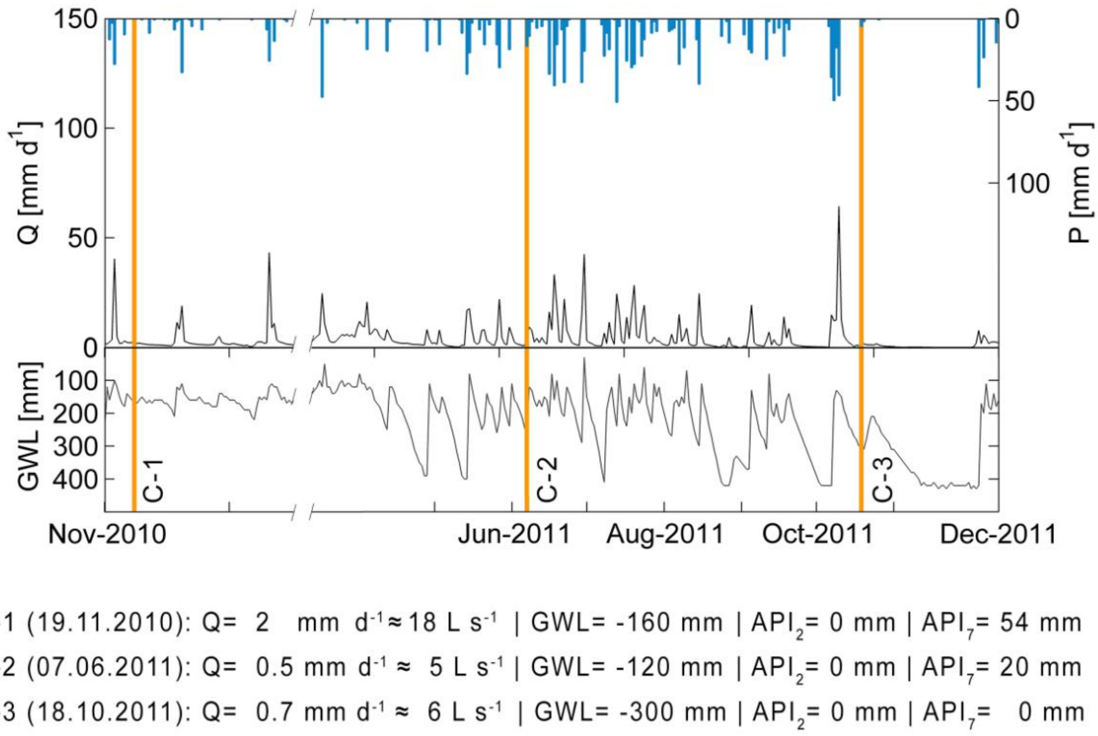

Figure 2 Precipitation (P), discharge (Q) and groundwater level (GWL) of WS04 between fall 2010 and 2011 with the sampling campaigns C-1, C-2 and C-3 (vertical lines). Text below is sampling campaign information on discharge, groundwater level relative to the surface and antecedent precipitation index (API) for 2 and 7 days.

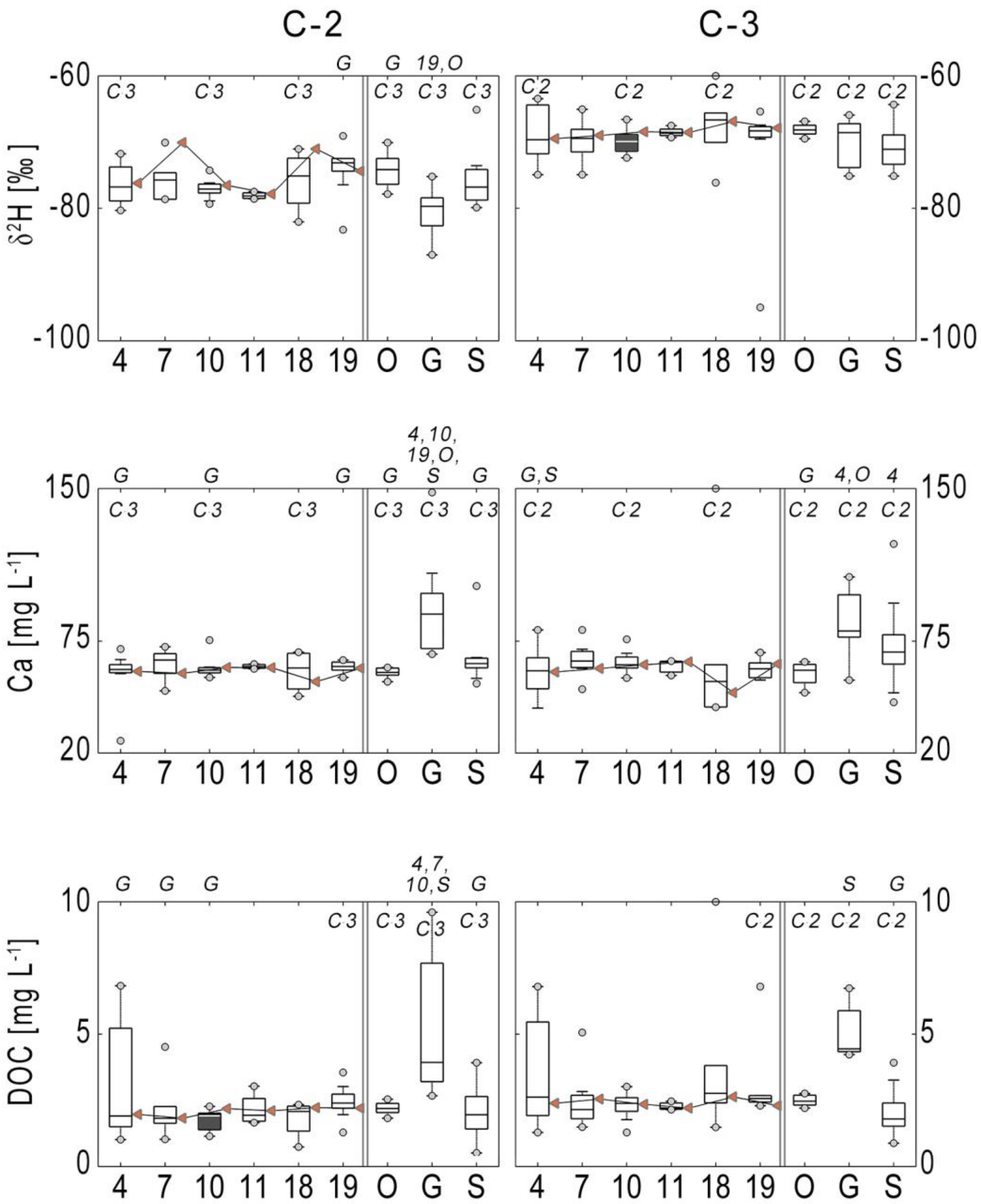

Figure 3a Isotopic and hydrochemical variables (rows) for each sampling campaign (columns: C2, C3). The x-axis indicate different groups, WS04 to WS19 (4 to 19), followed by outlets of all subcatchments (O), groundwater (G) and springs (S). The boxes show the range of values for different sample groups (showing the 25th, median, 75th percentile with whiskers of 10th and 90th percentile, and minimum and maximum as grey circles). The orange triangles, connected by a black line, indicate the values at the subcatchment outlet (missing triangles or lines are due to missing values). Italic letters in or on top of each box indicate significant difference in means (p<0.05) of the different datasets for: (I) temporal comparison of the means (C-2 and C-3) and (II) spatial comparison of WS, O, G and S. Black shaded boxes indicate a significant difference in means (p<0.05) of all stream samples of a subcatchment compared to its respective subcatchment outlet.

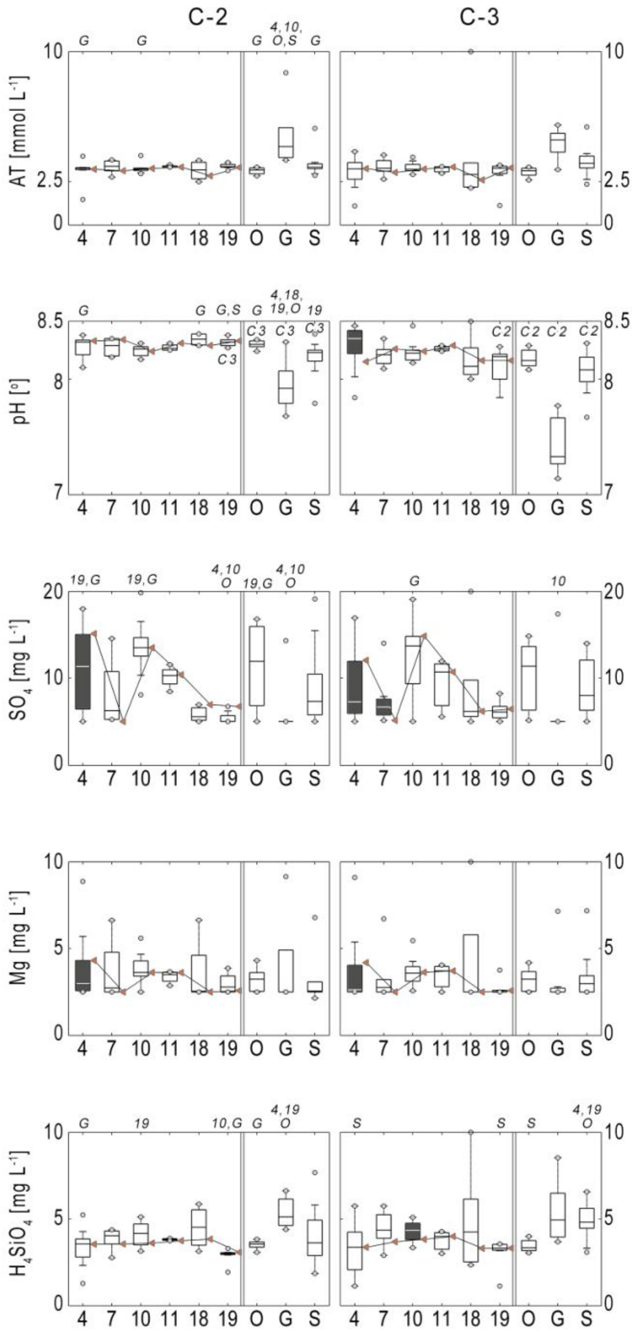

Figure 3b Hydrochemical variables (rows) for each sampling campaign (columns: C2, C3). The x-axis indicate different groups, WS04 to WS19 (4 to 19), followed by outlets of all subcatchments (O), groundwater (G) and springs (S). The boxes show the range of values for different sample groups (showing the 25th, median, 75th percentile with whiskers of 10th and 90th percentile, and minimum and maximum as grey circles). The orange triangles, connected by a black line, indicate the values at the subcatchment outlet (missing triangles or lines are due to missing values). Italic letters in or on top of each box indicate significant difference in means ($p<0.05$) of the different datasets for: (I) temporal comparison of the means (C-2 and C-3) and (II) spatial comparison of WS, O, G and S. Black shaded boxes indicate a significant difference in means ($p<0.05$) of all stream samples of a subcatchment compared to its respective subcatchment outlet.

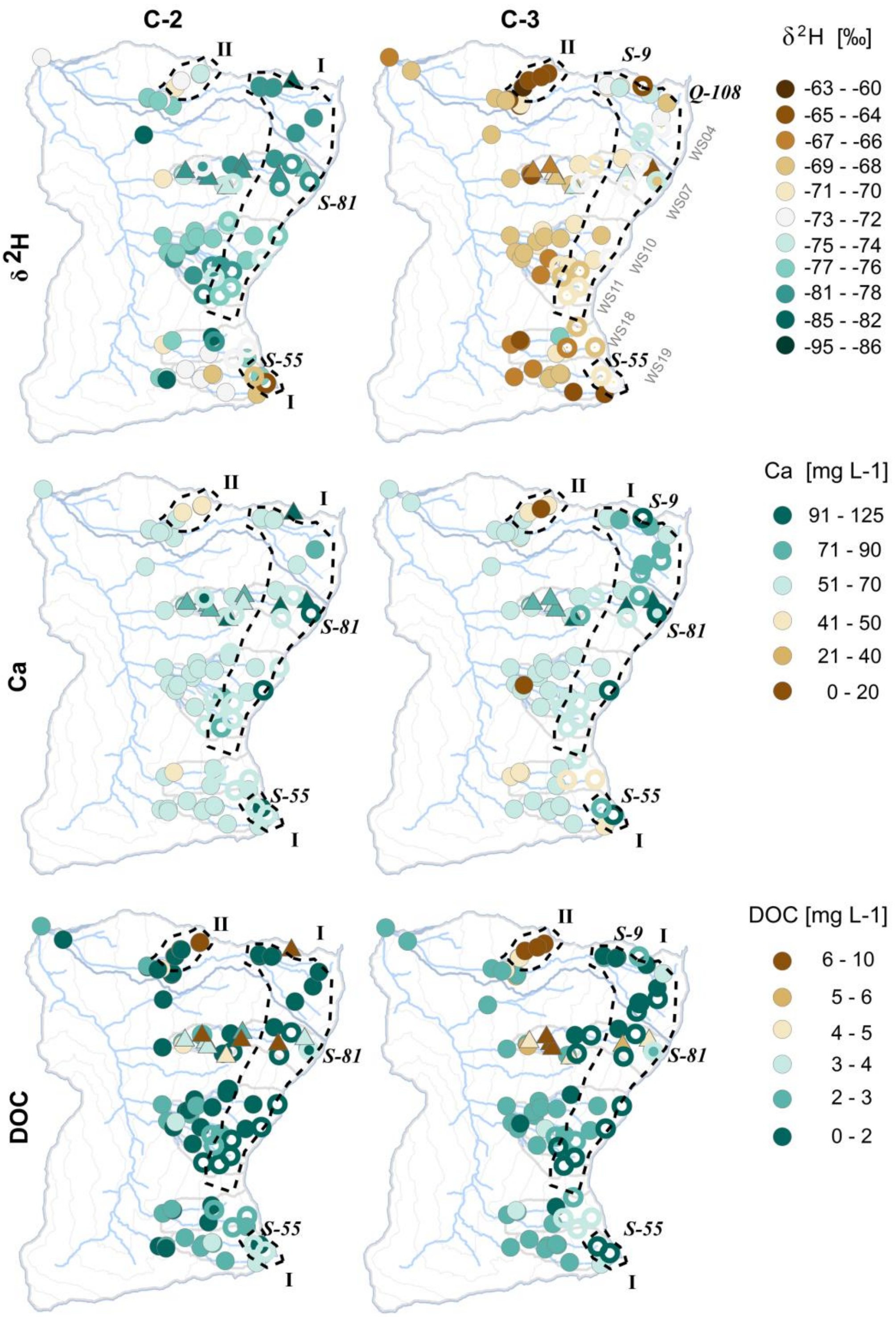

Figure 4 Spatial distribution of the isotopic and hydrochemical variables δ2H, Ca and DOC for C-2 and C-3: stream (filled circles), spring (open circles) and groundwater samples (triangles). Dashed lines with roman numerals I (upper spring zone) and II (tributary, i.e., drainage ditch from wetland) are regions with distinct composition. Letters indicate samples described in the text. Colours scheme from www.ColorBrewer.org.

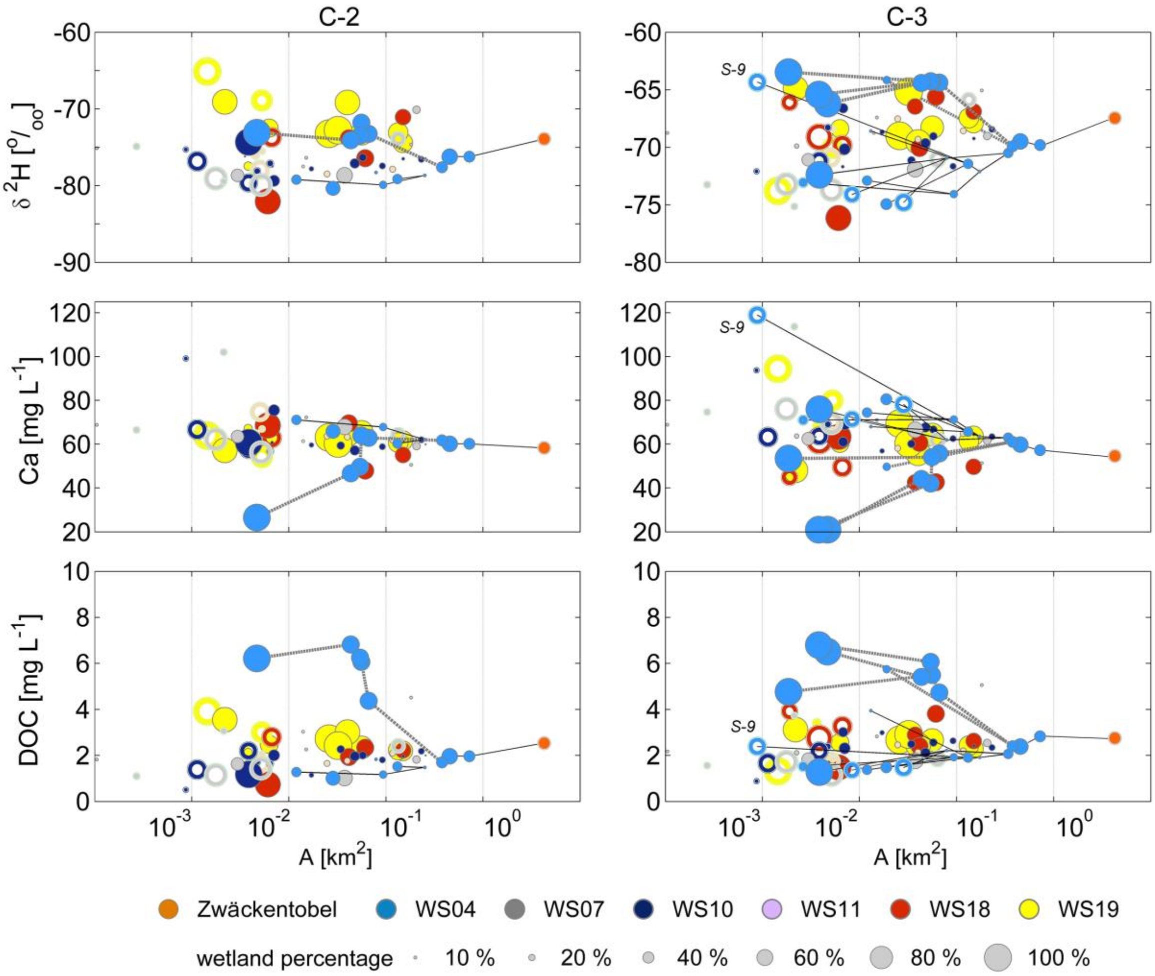

Figure 5 δ2H, Ca and DOC values for snapshot campaign C-2 and C-3 from the different sampling locations: stream (filled circles) and springs (open circles) represented as a function of their logarithmic catchment area. Symbols are scaled proportional to upslope wetland percentage. Black lines connect sampling points of WS04 along the main stream network of from the water divide to the catchment outlet. Grey lines connect sampling points of WS04 along the tributaries to the main stream.

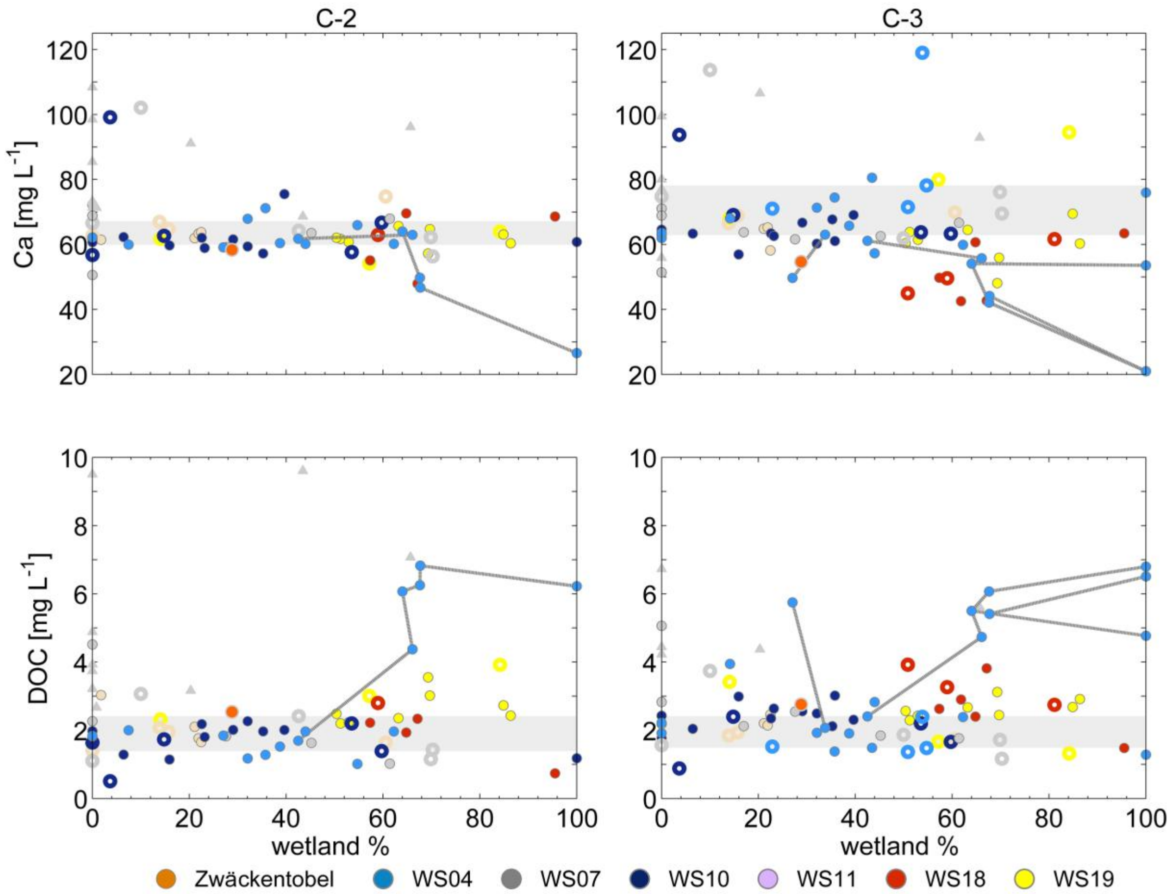

Figure 6 Ca and DOC concentrations for snapshot campaigns C-2 and C-3 as a function of their upstream wetland percentage for the different samples: stream (filled circles), springs (open circles) and groundwater (triangles). Grey lines connect sampling points of WS04 along the tributaries to the main stream. The grey shaded area indicates the variability of the spring signature based on the 25th and 75th percentile of Figure 3a.

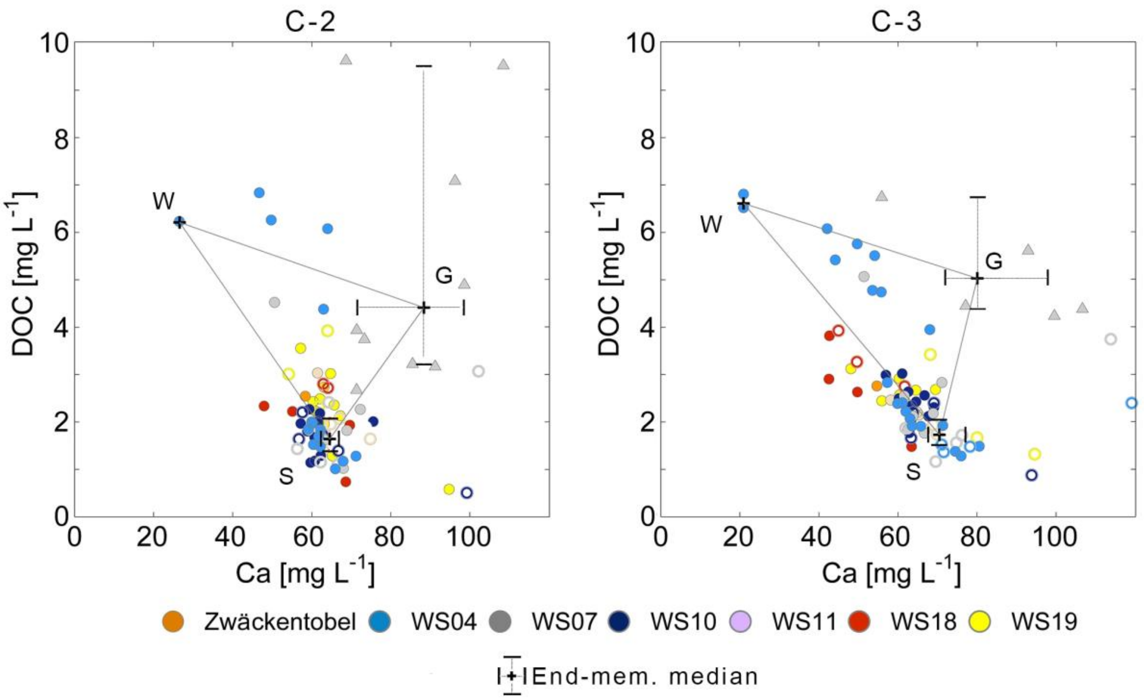

Figure 7 Bivariate representation of Ca and DOC for C-2 and C-3 with different samples: stream (filled circles), springs (open circles) and groundwater (triangles). End-members (+) are median of springs (S) wetland (W) and groundwater (G) samples each with their upper and lower quartiles (error bar).

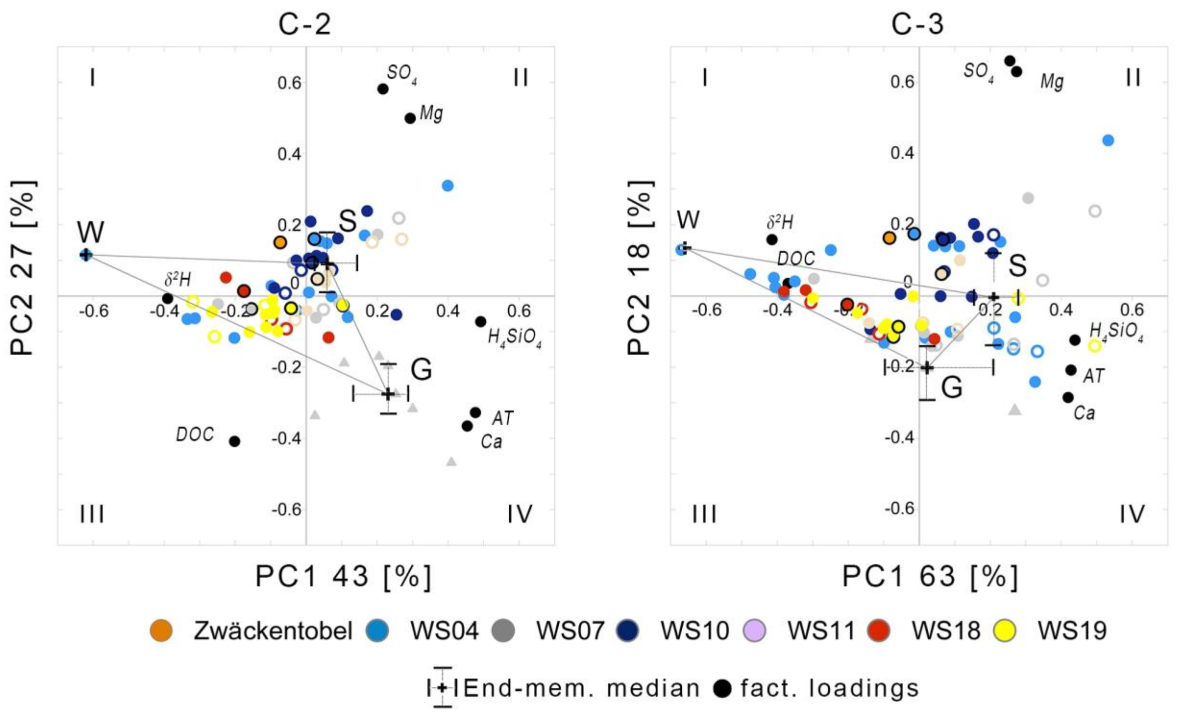

Figure 8 PCA-biplot of C-2 and C-3 with scores for stream (filled circles), springs (open circle) and groundwater samples (triangle) and correlated isotopic and hydrochemical loadings. ZT is the Zwäckentobel outlet. Quadrants are numbered with roman numerals. End-members (+) are median of springs (S) wetland (W) and groundwater (G) samples each with their upper and lower quartiles (error bar).